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Iron Precipitation upon Gettering in Phosphorus-Implanted Czochralski Silicon and its Impact on Solar Cell Performance

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***Abstract*—Phosphorus implantation can provide a direct route to a high-performing emitter, with no surface dead layer and improved blue response, and potentially higher open-circuit voltage. Here, iron precipitation during gettering is investigated in phosphorus-implanted, low-oxygen monocrystalline silicon and its impact on device performance evaluated. Previously, it has been shown that *higher* levels of initial iron contamination lead to *lower* final interstitial iron concentration after gettering with ion-implanted emitters, resulting in longer final bulk diffusion lengths in the more-highly contaminated materials. In this contribution, we show that despite longer bulk diffusion lengths, the open circuit-voltage of devices made from the highly iron-contaminated material can be strongly reduced. Using synchrotron-based X-ray fluorescence we reveal the presence of micron-sized iron precipitates in the near surface region. While not measured over wafer-sized areas, the density of these precipitates correlates with the annealing profile. Slow-cooling from the activation anneal and proceeding directly to a 620-750°C gettering anneal results in large precipitates that are indicated as the underlying cause for the disastrous open-circuit voltage. On the other hand, quickly cooling to room temperature and then re-inserting the wafers for gettering results in very small precipitates that do not appear to have significant detrimental affects on open-circuit voltage. It is thus critical to consider the precipitation behavior of iron during gettering of ion-implanted emitters – even in monocrystalline silicon – and during low-temperature annealing in general.**

***Index Terms*—emitter, gettering, implantation, iron, X-ray fluorescence**

I. Introduction

Implantation of phosphorus to form the emitter of silicon solar cells offers several advantages over a traditional CVD including good within-wafer, wafer-to-wafer, and run-to-run homogeneity, low emitter saturation current, high open-circuit voltage, and improved blue response. However, the goals of a traditional phosphorus diffusion also include gettering of lifetime-killing iron impurities, one mechanism being the relaxation gettering to phosphorus precipitates in the dead layer or at the surface [1]. Achieving high bulk minority carrier lifetimes after gettering is critical to cell performance, and the extent and mechanisms of gettering in ion-implanted emitters are currently under investigation [2].

Recently, surface photovoltage (SPV) measurements revealed that after gettering with ion-implanted emitters *higher* levels of initial iron contamination can lead to *lower* final interstitial iron concentration. The interstitial iron concentrations for wafers contaminated with $2 \cdot 10^{14}$ cm^{-3} were lower for each gettering condition than similar wafers that were prepared with a lower initial total iron concentration of 10^{13} cm^{-3}, suggesting that precipitation played a role in the gettering process. However, interstitial concentrations remain above the solid solubility in p-type silicon at the gettering temperature [3], [4]. Secondary-ion mass spectrometry indicates an anomalously high iron concentration just below the surface [2]. In correlation with this lower interstitial iron concentration, here we report normalized open-circuit voltages in fully processed ion-implanted cells that further indicate that precipitation might significantly affect iron behavior in ion-implanted emitters.

Attempts to locate precipitates with transmission electron microscopy (not shown) failed to discover any precipitates, in part because in monocrystalline silicon there are no obvious, immediately identifiable extended defects, such as grain boundaries, to direct investigation. We turn to synchrotron-based micro-X-ray fluorescence (f1-XRF) to investigate the precipitation behavior of iron in these ion-implanted samples.

f1-XRF offers both high-resolution, sub-100 nm in the hard X-ray regime, and relatively large sampling areas, typically on the order of 10^2-10^3 f1m^2. f1-XRF has proven useful in probing the behavior of iron in multicrystalline silicon especially [5], given its occurrence at readily observable grain boundaries [6] and dislocations [7]. The evolution of the iron distribution as a function of silicon solar cell processing has been investigated for *p*-type multicrystalline silicon with standard tube-furnace gettering and firing processes [8], for in-line gettering of red zone material [9], and in a systematic investigation of higher gettering temperatures by several authors [10], [11]. Iron precipitates in contaminated regions of *n*-type multicrystalline silicon ingots are also under investigation to better understand their performance impact [12].

Here, in phosphorus-implanted and gettered monocrystalline Cz wafers, we identify near-surface iron precipitates in samples subjected to various gettering treatments and correlate the precipitate distributions to the gettering conditions and the resulting impact on minority carrier diffusion length and open-circuit voltage [13].

II. Methods

Monocrystalline p-type (2.7-3.0 Ω-cm) silicon wafers were intentionally contaminated with iron to a total concentration of $2 \cdot 10^{14}$ cm^{-3} by immersing in an iron-containing solution and subsequent annealing at 940°C for 50 min for in-diffusion [14]. After contamination, the wafers were screened with a thin oxide and then ion-implanted on one side with a phosphorus dose of 10^{15} cm^{-2} at 50 keV. The wafers were cleaned and then the implant activated at 1000°C for a total of 40 min before cooling at 4°C/min for a gettering step at: (i) 750°C for 3.5 hr (ii) 620°C for 8 hr or (iii) quenched to room temperature (RT) from 895°C and then re-heated to 620°C for an 8 hr anneal, referred to below as the 750°C, 620°C, and RT + 620°C samples respectively. Further sample and cell preparation and SPV measurement details can be found elsewhere [2].

f1-XRF measurements were performed at the Advanced Photon Source beamline 2-ID-D [15] with a 200 nm spot size at 10 keV. Details on the analysis of iron-containing particles can be found in [8].

III. Results and Discussion

After gettering, SPV measurements indicate a strongly process-dependent diffusion length, as reported previously [2] and shown in Fig. 1a. Also shown are the diffusion length limitations imposed by the concentration of interstitial iron in these samples, measured by SPV using the Fe-B pair dissociation technique. The measured diffusion length is lower than the diffusion length limited by interstitial iron alone. This difference in diffusion lengths is attributable to other defects or recombination mechanisms (L_{diff} other) and is also plotted in Fig. 1a. The diffusion lengths of the 750°C and 620°C samples, 169 and 544 f1m respectively, are both largely limited by interstitial iron despite differing significantly in value, because of the varying efficacy of the anneals at reducing interstitial iron. On the other hand, the RT + 620°C sample is not significantly limited by interstitial iron, but still has a low diffusion length of 188 f1m, possibly attributable to a high density of precipitates in the bulk [2].

The open-circuit voltages (V_{oc}) of completed devices, normalized to reference devices made without intentional iron contamination, do not correlate with the diffusion lengths for these three process conditions (Fig. 1b). The 750°C and 620°C samples show low normalized V_{oc} while the RT + 620°C sample delivers an open-circuit voltage approaching that of the reference.

Synchrotron-based f1-XRF measurements offer an explanation for the relationship between V_{oc} and annealing treatment, providing direct evidence for iron precipitation after each of the gettering anneals. Iron is positively identified in each sample, including both the Fe K_α and K_β peaks. A weaker Cu signature is seen at each precipitate, and possible Zn is seen in the RT + 620°C sample. See [13] for details.

The RT + 620°C sample appears to contain smaller precipitates than the others, likely because of the rapid cool to room temperature. The rapid cool should result in a higher density of small precipitates, including many that are below the detection limit of the experimental setup ($4 \cdot 10^4$ atoms/pcp.), and possibly a larger amount of iron precipitated in the bulk. Similarly, the density of detectable precipitates in the 620°C samples is also higher than in the 750°C sample, consistent with a larger supersaturation at the lower gettering temperature. These observations will be compared against an iron precipitation and growth model [13].

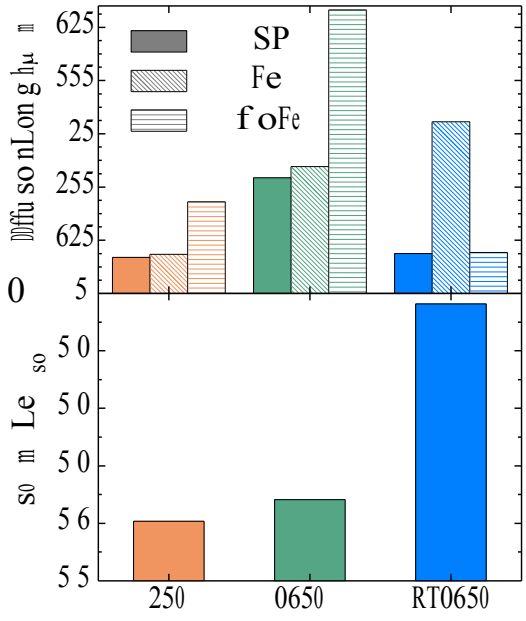

Figure 1. (a) The diffusion length after three different gettering processes is shown: as measured by SPV, as calculated from the measured interstitial iron concentration, and, from the difference between the two, the diffusion length limit imposed by other recombination pathways. (b) The open-circuit voltage measured on devices made from wafers having undergone the three gettering anneals.

IV. Conclusion

Iron precipitates are detected close to the surface after gettering of phosphorus-implanted monocrystalline wafers. Slow cooling from activation annealing temperatures to a moderate gettering temperature produces large precipitates, in some cases >1 f1m in size, that are likely the cause of the low open-circuit voltages found in devices made from these wafers. Large precipitates are avoided and simultaneously an adequately low interstitial iron concentration achieved by removing the samples from the furnace while at high temperature (here 895°C) and then subsequently re-inserting for a gettering anneal (RT + 620°C). Widespread precipitation is presumed to occur upon quenching to room temperature, and this hypothesis is supported by the f1-XRF observation of several nanoscopic precipitates just above detection limits. While the interstitial concentration is indeed low in the quenched and re-annealed sample, the diffusion length is significantly limited by a defect other than interstitial iron,

possibly recombination at the high density of iron precipitates. A tuned time-temperature profile that produces widespread precipitation but allows some ripening may ultimately produce the improved diffusion length and V_{oc} required for high-performing devices.

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